Diffusive and Convective Transport of Organics in Ion-Exchange Membranes

L MA*, L Gutierrez*, M Waqas*, A Verliefde*

* Particle and Interfacial Technology Group (PaInT), Faculty of Bioscience Engineering, Ghent University. Coupure Links 653, 9000 Gent, Belgium.

Summary:

The diffusive and convective transport of uncharged (i.e., phenazone, paracetamol, and theophylline) and charged organics (i.e., clobifric acid and atenolol) in ion-exchange membranes (IEMs), as well as the experimental validation of the solution-diffusion model were investigated in diffusion cells. The transport of uncharged organics from the feed to the receiving compartment in the absence of salt was purely diffusion-driven, while the presence of salt in the receiving solution side highly assisted the transport of organics, suggesting a convective transport by the drag of water molecule due to the osmotic pressure. The co-existence of salt hindered the transport of organics due to the smaller size of ions. The experimental validation of the solution-diffusion model showed that the model underestimated the uncharged solutes transport in IEMs. Monte Carlo analysis indicated that this discrepancy could not be ruled out even after considering experimental errors. The method for determining contact angle and the definition of diffusive hindrance factor may lead to these discrepancies. This study contributes to the field of selective organics/inorganics separation using IEM technologies (i.e., electrodialysis, reverse and assisted-reverse electrodialysis) in the treatment and resource recovery of organics-rich industrial wastewater.

Keywords: Ion-exchange membrane; organic transport; modelling

Introduction

Selective separation of organic and inorganic components is of great value in industrial wastewater treatment, to improve recovery of both organics and inorganics (Han et al. 2016). Ion-exchange membrane (IEM) technologies could be the key to addressing this issue. However, only a limited number of studies have focused on separation mechanisms of organics and inorganics in complex streams by IEMs (Zhang et al. 2011). Also, the transport mechanisms of organics through IEM has often been overlooked. Therefore, this research aims to investigate the convective transport of organics, as well as to build a predictive model for diffusive transport of uncharged organics in IEMs.

Material and Methods

Five pharmaceutical compounds (phenazone, paracetamol, and theophylline as uncharged organics; clobifric acid and atenolol as negatively and positively charged organics, respectively) and 4 commercial IEMs (Fujifilm) were selected to perform the diffusion and convection experiments in diffusion cells. In the diffusion experiment, the organics concentration gradient across the membrane was the only driving force applied for solute transport, while salt (NaCl) gradient was applied to the convection experiments. The process of the transport of uncharged organic solutes in dense membranes has been described by the solution-diffusion model (Eq. 1) (Verliefde et al. 2013),

$$J_s = -\frac{D_{s,m} \cdot \emptyset \cdot \varepsilon}{\Delta x} \cdot \Delta C \qquad \text{(Eq. 1)}$$

Where J_s is the solute flux, $D_{s,m}$ is the diffusion coefficient of solute in the membrane, ϕ is the partition coefficient, ε is the membrane porosity, ΔC is the concentration difference across the membrane, Δx is the thickness of the membrane.

$D_{s,m}$ was determined by ^{1}H NMR. ϕ was determined as the ratio of solute radius r_s and membrane pore size r_p. The solute-membrane affinity (ΔG) was determined via contact angle. Δx was measured by ESEM. The flux data obtained in the diffusion experiments and the experimentally determined parameters were used to fit the solution-diffusion model to solve for r_p and ε. A predictive model was built and validated by comparing predicted flux with measured flux for other solutes. Sensitivity

analysis was performed using Monte Carlo simulation to elucidate the difference between model-predicted and measured flux.

Results and Conclusions

The linear increase of phenazone flux (R^2=0.92) as function of its concentration difference (Fig. 1a) indicated **purely (solution-) diffusion driven transport** of phenazone. Similar trends were observed in the other membranes under the same condition with other organic solutes and membranes in terms of J_s /ΔC (Fig. 1b). It also showed a higher transport of uncharged organics in anion-EMs (AEMs) than cation-EMs (CEMs) possibly due to the higher cross-linking and lower affinity to organics of CEMs. A correlation between transport and molecular weight was observed in all IEMs following the trend: paracetamol > theophylline > phenazone. With the **co-existence of salt, the transport** of atenolol (positively charged organic) **was hindered** and could be explained by the ease of the transport of NaCl (Fig. 1c). A **faster transport** was observed when the salt was present in the receiving compartment **due to the drag of water molecules** under osmotic pressure, i.e., salt gradient (Fig. 1d).

Subsequently, the solution-diffusion model was applied to predict the diffusion flux of uncharged organics in IEMs. As shown in Fig. 1a, the modeled slope (J_s /ΔC) of phenazone in CEM I was 14% lower than the experimental slope, which showed the same prediction result, as in the **underestimation of the model to the transport of the solutes**. Finally, Monte Carlo analysis indicated that the **discrepancy** between modeled and measured fluxes **could not be ruled out** even after considering experimental errors (Fig. 1a). The method for determining **contact angle** and the definition of **diffusive hindrance factor may lead to these discrepancies**, requiring further investigation.

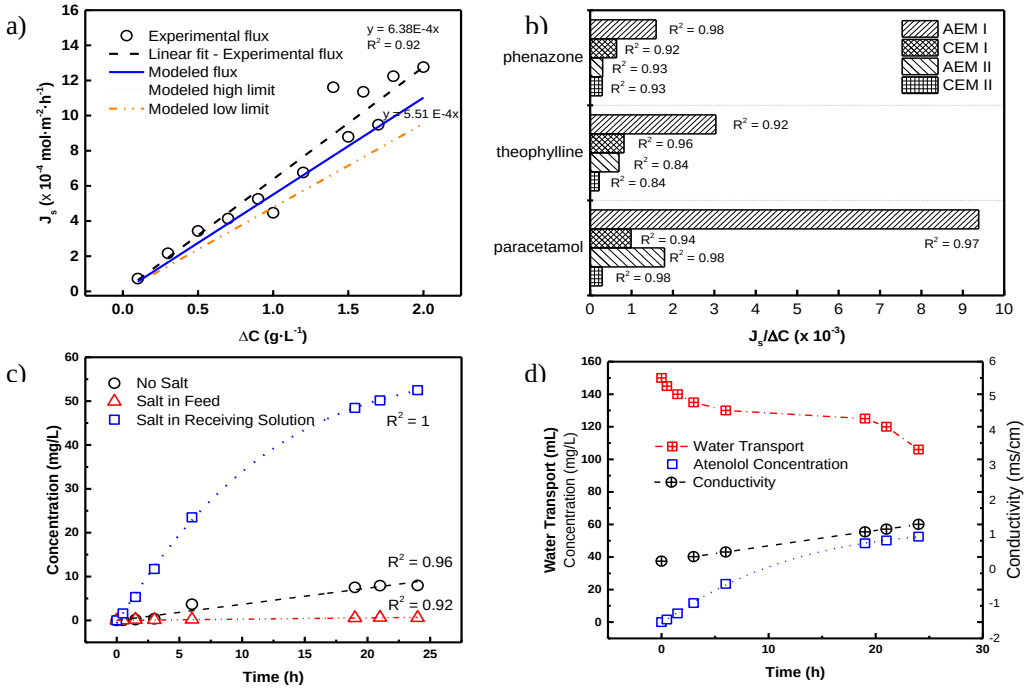

Figure 1 a) Modelling of the transport of phenazone in CEM I. **b)** Uncharged organic solute flux over concentration gradient (J_s /ΔC) in IEMs. **c)** Influence of the presence of salt on the transport of atenolol in CEM I. **d)** Water volume and conductivity in the feed side and the corresponding atenolol concentration in the receiving solution side in CEM I.

References

Han, L., Galier, S. (2016), Roux-de Balmann, H., Transfer of neutral organic solutes during desalination by electrodialysis: Influence of the salt composition, *J. of Membr. Sci.*, 511, 207-218.

Verliefde, A.R. (2013), Vander Meeren, P., Vander Bruggen, B., Encyclopedia of Membrane Science and Technology, *John Wiley and Sons*.

Zhang, Y., Pinoy, L. (2011), Meesschaert, B., Van der Bruggen, B., Separation of small organic ions from salts by ion-exchange membrane in Electrodialysis, *AIChE J.*, 57, 2070-2078.